

Stimulated Raman scattering in micrometer-sized droplets: time-resolved measurements

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Received January 12, 1988; accepted March 18, 1988

Time-resolved measurements of elastic scattering and stimulated Raman scattering (SRS) in micrometer-sized water and carbon tetrachloride droplets irradiated with a pulsed, frequency-doubled Nd:YAG laser (pulse width 8 nsec, $\lambda = 532$ nm, peak intensity 51 GW/cm²) are reported. Elastic scattering of light is instantaneous within our measurement error, estimated to be <3 nsec. On the other hand, the first Stokes shift in water and multiple-order (through ninth-order) Stokes shifts in carbon tetrachloride are delayed from the elastically scattered light by 5–7 nsec. The delay in SRS is apparently a consequence of structure resonances within the droplet, which acts as an optical cavity with relatively high Q . Quasi-periodic peaks in SRS spectra of water droplets are shown to be associated with elastic-scattering structure resonances having the same mode order.

Measurements of the spectral characteristics of stimulated Raman scattering (SRS) from micrometer-sized water and carbon tetrachloride (CCl₄) drops have previously been reported.^{1,2} The spectra for water drops show quasi-periodic peaks within the broad spontaneous Raman bandwidth of bulk water, and it has been suggested that they are associated with structure resonances (sometimes called morphology-dependent resonances) within the drop.¹ For CCl₄ drops, multiple-order Stokes shifts were observed.² In this Letter we present time-resolved measurements of the elastic scattering and SRS from water and CCl₄ drops. We also present spectral measurements of SRS from accurately sized water droplets and identify regularly spaced peaks in the spectra with elastic-scattering structure resonances within the drop.

A schematic diagram of our experimental arrangement is shown in Fig. 1(a). Green light from a frequency-doubled laser is focused onto droplets that scatter elastic (green) and inelastic (red-shifted SRS) light into the spectrometer. Part of this light is reflected onto a one-dimensional array detector (PDA) by a beam splitter (BS2) for measurement of its spectral content. The remaining scattered light is combined with a delayed (green) light pulse from the reference beam and passed through the exit slit onto a photomultiplier tube (PMT). The PMT signal is then fed to a transient digitizer, and the resulting signal traces are displayed on a CRT for measurement of time delay between scattered and reference beams [Fig. 1(b)]. The calculated time delay between these two beams, taking into account the speed of light and path-length difference and assuming that droplet

scattering is instantaneous, is 54 nsec. Delay of the reference beam by this comparatively long time (compared with the laser pulse length of 8 nsec) allows for measurement of scattered light and reference beam with a single detector. This arrangement permits time-resolved and spectrally resolved measurements of scattered light on single laser shots, which we found necessary to eliminate undesirable pulse waveforms on some single shots.

As a check on the credibility of the method for making time-resolved measurements, we first replaced the drops with a cell containing liquid CCl₄. A mirror was placed in an appropriate position to reflect the elastic and forward-scattered inelastic (SRS) radiation into the spectrometer and photomultiplier tube. Measured time-of-arrival differences between light of the reference beam and the elastic and first Stokes shift of the ν_1 (458-cm⁻¹ shifted) Raman line were within 1 nsec of the delay expected for the path-length difference (54 nsec), suggesting that both elastically scattered light and SRS in bulk CCl₄ are nearly instantaneous, as expected.

We then introduced droplets into the laser focal region and made time-resolved and spectrally resolved measurements for single laser shots at laser intensities just below that required for aerosol-induced breakdown.³ Our time-resolved measurements for 26- and 68- μ m-diameter water drops and 66- μ m-diameter CCl₄ drops are shown in Fig. 2. As for bulk, elastic scattering is instantaneous for both liquids. However, unlike in the bulk, the SRS light for the first Stokes shift for water and multiple-order Stokes shifts for the strongest Raman line (ν_1) of CCl₄ are all delayed by

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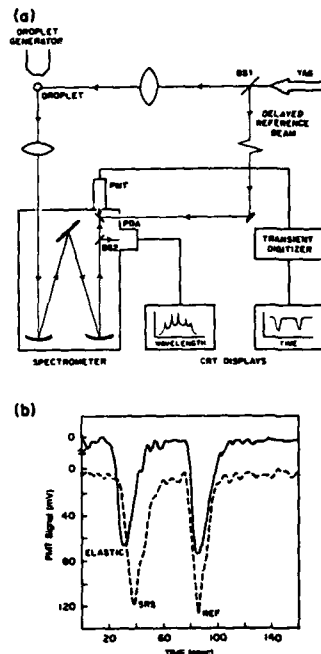


Fig. 1. (a) Schematic of the experimental setup used for measuring time dependence and spectral content of elastic and inelastic (SRS) scattering in small droplets. (b) Typical transient digitizer traces of the PMT signal. The time delay of elastic scattering and SRS is determined by measuring peak-to-peak time differences between the scattered and reference beam pulses.

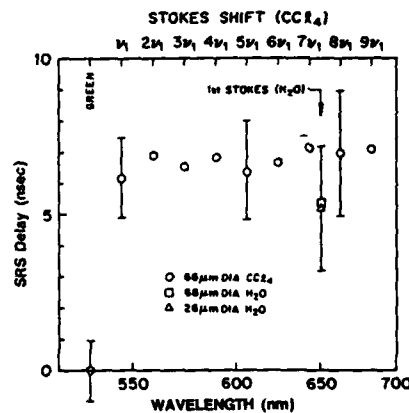


Fig. 2. Time-resolved measurements of elastic scattering and SRS from water and CCl_4 droplets. Time delays for the first Stokes shift for water drops and for multiple (through ninth-order) shifts for CCl_4 drops are shown. The laser pulse width is about 8 nsec; the peak intensity is about 1 GW cm^{-2} . Data points depict averages of 25–50 single laser shot measurements of the delay together with typical one standard deviation. Absolute errors arising from differences in the laser and SRS signal pulse widths and from finite detector time response are estimated to be not more than an additional $\pm 2 \text{ nsec}$.

about 5–7 nsec. Our finding that the delay for water and CCl_4 is about the same suggests that the drop shape (which enables resonances to exist), not the drop material, is instrumental in causing the delay. Our finding that the delay in the multiple-order Stokes shifts in CCl_4 are all about the same suggests that all multiple ν_1 shifts are excited simultaneously.

It is noteworthy that higher-order Stokes shifts of CCl_4 (fourth-order ν_1 shifts and higher) occasionally show complicated time dependence, wherein the SRS is emitted in two or three bursts delayed from the elastic scattering by as much as 30 nsec. These data were not included in the delays reported here. We also observed that time delays for mixed SRS modes involving combinations of the strong ν_1 Raman line and weaker ν_2 (218 cm^{-1} shift) and ν_4 (314 cm^{-1} shift)

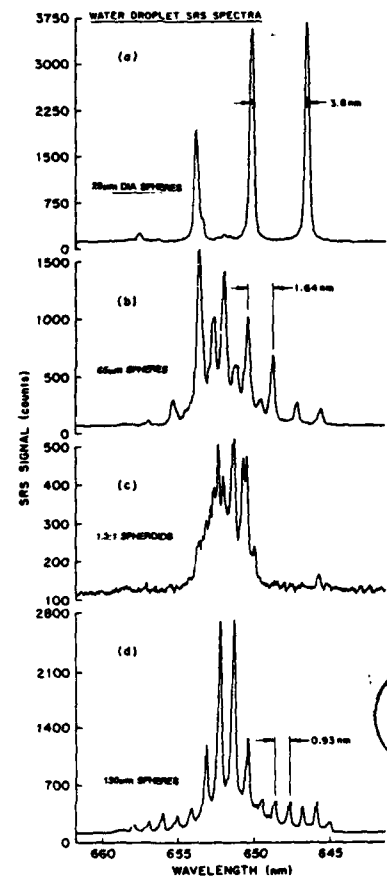


Fig. 3. Single-shot SRS spectra of water drops irradiated with green light from a pulsed laser with peak intensity $\sim 1 \text{ GW cm}^{-2}$. Spherical drops range in size from 29- to 130- μm diameter [(a), (b), (d)]. The peaks are quasi-periodic. Spectra for spheroids (c), obtained by detuning the droplet generator from the resonant frequency used in (b) to generate spheres, show a plethora of resonance peaks. The spheroids have nearly the same volume as spheres in (b); their axial ratio was estimated by viewing them through a microscope with 200 \times magnification.

A-1 21

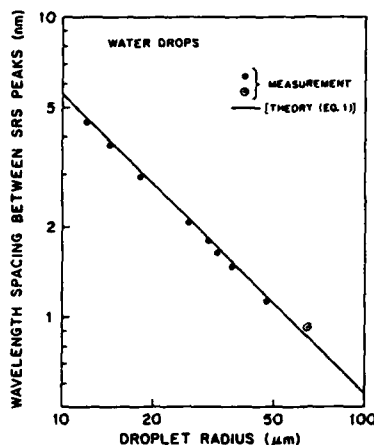


Fig. 4. Measured period of peaks appearing in the SRS spectra of spherical water drops (see Fig. 3) as a function of measured drop size. Measurement errors are $\pm 5\%$ in wavelength, $\pm 15\%$ in size for the open data point, and $\pm 2\%$ in size for the filled data points. The measurements are in good agreement with the theoretical prediction [Eq. (1)], which is compelling evidence that there is a unique correspondence between SRS peaks and elastic scattering structure resonances within the drops.

lines, i.e., $\nu_1 + \nu_2$, $2\nu_1 + \nu_2$, $\nu_1 + \nu_4$, and $2\nu_1 + \nu_4$, appeared to be delayed 1–3 nsec more than the ν_1 shifts. However, there are large statistical errors in these data because of small SRS signals and because some mixed-mode SRS signals occur infrequently (in fewer than one of five laser shots).

All measurements of the time delay of SRS reported here are for laser intensities just below the threshold for aerosol-induced breakdown. However, we did find that adjustment of the laser intensity changes the observed time delay. When the laser intensity was increased above the breakdown threshold, the time delay in SRS was substantially reduced. This finding is consistent with 1) our observation that above breakdown threshold SRS is generated only during the rising part of the laser pulse, since generation of plasma internal to the drop quenches SRS, and 2) our conjecture that higher laser intensity causes resonances that support SRS to build up faster, resulting in less time delay of SRS.

Although it is generally believed that SRS emissions in small drops correspond to structure resonances in the drop,^{1,2} no actual identification of resonances has been made. To contribute to the solution of this problem we measured single-shot SRS spectra in water drops as a function of drop size, as shown in Fig. 3. Drop size was determined within 2% accuracy by measuring the vibrating orifice generator frequency and by weighing timed collection of the counted number of droplets. Several SRS peaks appear within the broad spontaneous Raman linewidth (as found previously in SRS¹ and spontaneous Raman⁴⁻⁶ spectra), and these peaks have a quasi-periodic structure.

If these peaks are associated with corresponding structure resonances in elastic scattering of the same order l , then they should have wavelength separation given by the asymptotic relation⁷

$$\Delta\lambda = \frac{\lambda^2}{2\pi r} \frac{\arctan(n^2 - 1)^{1/2}}{(n^2 - 1)^{1/2}}, \quad (1)$$

where r is the drop radius ($r \gg \lambda$) and n is the droplet refractive index. Our measurements of the separation of peaks $\Delta\lambda$ (done by applying a fast-Fourier-transform method to the spectral data) versus drop radius r are shown compared with the Eq. (1) prediction in Fig. 4. Considering that there is no free-fitting parameter in Eq. (1), the agreement is remarkably good. This is compelling evidence that the SRS emissions seek out structure resonances in the drop, with each successive peak corresponding to elastic-scattering resonances of sequential mode number n but of the same mode order l . We believe that the pairs of doublet peaks appearing in some spectra for spheres [Fig. 3(b)] correspond to transverse electric and transverse magnetic modes, both of which have the same period.⁷ Occasionally additional peaks (not shown here) are observed that may correspond to resonances of different order; alternatively, these additional peaks may derive from cooperative scattering effects, with SRS coming from multiple drops, or from drops of different sizes, with each drop supporting different resonances. Spheroidal shapes [Fig. 3(c)] cause a plethora of resonance peaks, in qualitative agreement with theoretical prediction.⁸

We suggest that the delay of SRS in small drops is a consequence of the finite time required to build up resonances that support SRS. The droplets act as electromagnetic cavities with Q (energy stored/power gain per cycle = time delay of SRS for laser intensity used/period per cycle) $\approx 3 \times 10^6$. The SRS spectra are normally dominated by one set of quasi-periodic peaks, suggesting that for a given droplet size and refractive index, structure resonances of a particular width and mode order dominate over all others.

The research of A. Biswas, P. Chýlek, R. L. Armstrong, and H. Latifi was partially supported by U.S. Army Research Office contract DAAL 03-87-K-0144, AND K-C023.

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